$$D(M^+-C_nH_{2n}) \geq 17.8n + \Delta H_f(C_nH_{2n}) \text{ (kcal/mol)} \quad (2)$$

considering $n = 4$, if the C_4H_8 ligand is 2-butene ($\Delta H_f = -3$ kcal/mol), the metal-olefin bond strength must be at least 68 kcal/mol. For a metallacyclopentane structure, each metal-carbon bond must be at least 69 kcal/mol strong.[17] A bis-ethylene ($\Delta H_f = 25$ kcal/mol) structure requires the metal-olefin bond to exceed an average of 48 kcal/mol. While these metal-ligand bond strengths are all high, they are not sufficiently unreasonable to permit any of these structures to be excluded on thermodynamic grounds. Fragmentation and ligand displacement studies are in progress to elucidate the mechanisms and structures involved in these interesting reactions.

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(17) Estimating ΔH_f(1,4-butanediyl) $\approx 2\Delta H_f(n\text{-}C_4H_9^\bullet) - \Delta H_f(n\text{-}C_4H_{10})$.

Binding of 2,2'-Bipyridine to the Dirhodium(II) Tetraacetate Core: Unusual Structural Features and Biological Relevance of the Product $Rh_2(OAc)_4(bpy)$

Spiros P. Perlepes,[1a,d] John C. Huffman,[1b] John H. Matonic,[1c] Kim R. Dunbar,*[,1c] and George Christou*[,1a]

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received September 24, 1990

Dirhodium tetracarboxylate complexes have attracted considerable interest due to their catalytic[2] and antitumor activity.[2,3] We have long been intrigued by the latter, the ability of $Rh_2(O_2CR)_4$ complexes to prolong the survival times of tumorous mice.[3] The mechanism of action is unknown, but it has been suggested to be inhibition of DNA replication, involving $Rh_2(O_2CR)_4$ binding directly to DNA bases.[4,5] For the better understood antitumor agent *cis*-$(NH_3)_2PtCl_2$, the primary DNA-binding mode is loss of the two Cl^- ions and intrastrand Pt attachment to the N7 atoms of two adjacent guanine bases.[6] The same is considered possible for the Cp_2MX_2 (M = Ti, V, Nb, Mo; X = halide) complexes and certain other metal-based antitumor agents.[7] The d(pGpG) unit thus acts as a bidentate chelate group. Conventional wisdom would suggest that $Rh_2(OAc)_4$ could not bind in a similar fashion, since the two labile (axial) sites are at opposite ends of the molecule. It might, therefore, be concluded that $Rh_2(OAc)_4$ binds to a single base or is akin to *trans*-$(NH_3)_2PtCl_2$, which binds to two nonadjacent DNA bases having one or more intervening nucleotides. We wondered whether such a conclusion is necessarily sound and whether $Rh_2(OAc)_4$ could indeed bind in a similar fashion to *cis*-$(NH_3)_2PtCl_2$.[8] A search of the Rh literature failed to unearth a $Rh_2(O_2CR)_4$ unit bound to a single bidentate nitrogen chelate.[9] We have therefore sought such a species using a bidentate group (2,2'-bipyridine; bpy) to mimic the "chelating" ligation of adjacent guanine bases. We herein describe the results of this study.

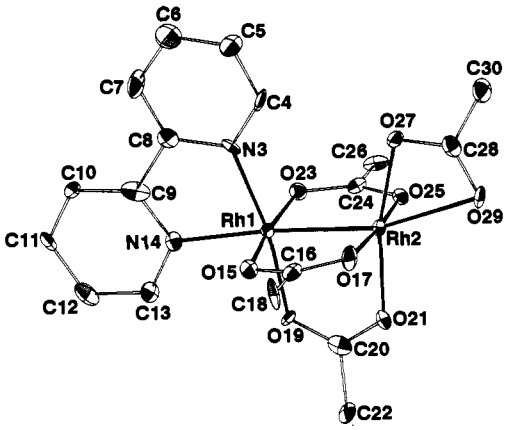

Figure 1. ORTEP representation of complex **1**. Selected bond lengths (Å) and angles (deg): Rh1-Rh2, 2.475 (2); Rh1-O15, 2.050 (8); Rh1-O19, 2.033 (7); Rh1-N3, 2.039 (9); Rh1-N14, 2.120 (10); Rh2-O17, 2.038 (8); Rh2-O21, 2.034 (8); Rh2-O25, 2.043 (8); Rh2-O27, 2.051 (8); Rh2-O29, 2.466 (8); Rh1-Rh2-O29, 163.5 (2); Rh2-Rh1-N14, 175.1 (3); C28-O27-Rh2, 99.9 (7); O27-Rh2-Rh1, 106.9 (2); O27-Rh2-O29, 57.1 (3); N3-Rh1-N14, 80.0 (4).

A wine-red solution of $Rh_2(OAc)_4 \cdot 2MeOH$ in MeCN was treated with 1 equiv of bpy. Following overnight storage at ambient temperature, green crystals of $Rh_2(OAc)_4(bpy)$ (**1**) were collected in 35-42% yield.[10a] A similar reaction with 2 equiv of bpy also gave green crystals of **1**, as did warming of the latter reaction solution to ~40 °C for a few hours. The unusual

(1) (a) Indiana University Chemistry Department. (b) Indiana University Molecular Structure Center. (c) Michigan State University. (d) On sabbatical leave from the University of Ioannina, Greece.

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(10) (a) Calculated for $C_{18}H_{20}N_2O_8Rh_2$: C, 36.14; H, 3.37; N, 4.68. Found: C, 35.6; H, 3.2; N, 4.4. (b) Crystal data: $C_{18}H_{20}N_2O_8Rh_2$, triclinic, $P\bar{1}$, $T = -172$ °C, $a = 9.883$ (3) Å, $b = 13.078$ (5) Å, $c = 8.323$ (2) Å, $\alpha = 97.02$ (2)°, $\beta = 106.90$ (1)°, $\gamma = 94.29$ (2)°, $V = 104.55$ Å^3, $Z = 2$, $6° \leq 2\theta \leq 45°$, unique data = 2636, observed data = 1959, $F > 2.33\sigma(F)$. The structure was solved by direct methods (MULTAN) and Fourier techniques and refined by full-matrix least squares. All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters, and they were included and refined isotropically in the final cycles. Final R (R_w) = 4.72% (4.50%).

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structure[10b] of **1** is shown in Figure 1. Two Rh^{II} centers are bridged by three $\eta^1:\eta^1:\mu_2$ AcO^- groups across a somewhat long Rh–Rh single-bond distance of 2.475 (2) Å.[2] A chelating bpy and a chelating AcO^- are bound to Rh1 and Rh2, respectively. The chelating AcO^- is asymmetrically ligated (Rh2–O27, 2.051 (8) Å; Rh2–O29, 2.466 (8) Å) as a consequence of the axial/equatorial location of O27 and O29; such asymmetrically chelating carboxylates are extremely rare,[11] symmetrical chelating being much more common.[12] Note that restrictions imposed by the four-membered chelate ring prevent O29 from occupying the true axial position (Rh1–Rh2–O29, 163.5 (2)°). The two Rh1–bpy linkages are also different (Rh1–N3, 2.039 (9) Å, Rh1–N14, 2.120 (10) Å) although to a lesser degree. The molecule possesses virtual C_s symmetry (mirror plane: N3, N14, Rh1, Rh2, O27, O29). It is reasonable to propose that complex **1** forms by initial binding of one bpy nitrogen (N14) to the axial position of Rh1 followed by binding of N3 to the equatorial position; the latter requires displacement of one equatorial acetate oxygen atom, which may then conveniently provide axial ligation at Rh2.

Conductivity measurements in CH_2Cl_2 show **1** to be a nonelectrolyte (Λ_M = 2S·cm²·mol⁻¹). The ^1H NMR spectrum of a freshly prepared solution in CD_2Cl_2 shows three methyl singlets at δ values of 1.67, 2.13, and 2.16 ppm in a 2:1:1 integration ratio, respectively, consistent with retention of the C_s-symmetry solid-state structure on dissolution. In the aromatic region, eight resonances (two slightly overlapping) are observed in the 7.46–9.64-ppm range, again consistent with the inequivalence of the two bpy rings under C_s symmetry. Two $\nu_{as}(COO)$ bands (1578, 1561 cm^{-1}) and two $\nu_s(COO)$ bands (1440, 1426 cm^{-1}) are observed in the IR spectrum (Nujol mull). The bands at 1578 and 1426 cm^{-1} are assigned to the bridging AcO^- groups, and those at 1561 and 1440 cm^{-1} to the chelating AcO^- group.[13] The UV/vis spectrum of a CH_2Cl_2 solution of **1** shows several features, with λ_{max}/nm (ϵ_M/L·mol⁻¹·cm⁻¹) values of 609 (350), 446 (2110), 426 (2005), 300 (19085), 276 (20760), and 244 (16710). $Rh_2(O_2CR)_4L_2$ (L = monodentate axial ligand) complexes usually display four bands near 600, 450, 250, and 220 nm,[1] but the greater number of bands for **1** is reasonable, given its lower symmetry. Cyclic voltammetric measurements on complex **1** reveal only an irreversible oxidation in CH_2Cl_2 (~0.45 V vs ferrocene).

From a purely inorganic viewpoint, the structure of **1** is novel for a Rh^{II}_2 compound in several ways, particularly its high asymmetry, the presence of only three bridges, and the occurrence of two different types of carboxylate coordination (bridging and chelating).[2] It is possible that the different coordination environments of the two metals will result in differing reactivity characteristics. From the biological viewpoint that stimulated this work, the identification of **1** firmly establishes that the $Rh_2(OAc)_4$ core can indeed readily bind to a chelating N ligand while resisting incorporation of a second chelating group (under the conditions used to date). If bpy is accepted as a reasonable model for chelation by two adjacent guanine groups, the identity of **1** suggests that the binding of $Rh_2(OAc)_4$ to DNA may be similar to that established for *cis*-$(NH_3)_2PtCl_2$ and that their antitumor activity may thus have a similar mechanism. Indeed, this possibility that $Rh_2(OAc)_4$ binds to DNA through more than just the axial sites is consistent with the observations of Howard et al.,[4d] who noted "because the inhibitory effects of rhodium(II) carboxylates are not reversible, by resuspension in fresh medium, it seems unlikely that reversible axial ligation reactions between the rhodium(II) dimer and biological ligands could account for the observed biological activity".

The identification of complex **1** now encourages us to move on to the logical second phase of this work, the attempted crystallization and structural characterization of an adduct between $Rh_2(OAc)_4$ and d(pGpG), as accomplished for *cis*-$(NH_3)_2PtCl_2$.[14]

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Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for **1** (3 pages). Ordering information is given on any current masthead page.

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Nickel(0)-Catalyzed Synthesis of Substituted Phenols from Cyclobutenones and Alkynes

Mark A. Huffman[1] and Lanny S. Liebeskind*[,2]

Department of Chemistry, Emory University
Atlanta, Georgia 30322

Received October 31, 1990

The reaction of strained small-ring organic compounds with unsaturated moieties via transition metal induced ring cleavage has been used to advantage in convergent syntheses of a variety of substituted five- and six-membered-ring structures.[3-16] An analogous reaction of substituted cyclobutenones with alkynes via the η^2-vinylketene (**1**) or η^4-vinylketene (**2**) metallic intermediates shown in Scheme I could provide a direct route to highly substituted phenols. All of the key steps in the scheme have been observed recently as discrete stoichiometric processes. Insertion of $ClRh(PPh_3)_3$ into cyclobutenones gave metallacycles of type **1** which did not react productively with alkynes,[17] while (η^5-indenyl)$Co(PPh_3)_2$ reacted to provide η^4-vinylketene complexes of type **2**, which upon heating with alkynes yielded phenols in some cases.[18] Herein is documented the first *metal-catalyzed* coupling of cyclobutenones and alkynes directly providing substituted phenols under mild conditions in good yields.

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